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(54) DEHYDROGENATION OF HYDROCARBONS

(71) We, AMERIPOL, INC., a Corporation organized under the laws of the State of Delaware, United States of America, of 1717 East Ninth Street, Cleveland, State of Ohio, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to a process for dehydrogenating hydrocarbons. More particularly, this invention relates to the oxidative dehydrogenation of hydrocarbons in the presence of oxygen and a catalyst.

Oxidative dehydrogenation processes have been employed to convert saturated and/or unsaturated hydrocarbons to more highly unsaturated hydrocarbons through removal of hydrogen from such hydrocarbons by combination with oxygen to form water and the unsaturated product in the presence of a catalyst. Catalyst systems have heretofore been proposed to increase the selectivity of the process to produce the desired product and the conversion per pass of the feed stream thereby maximizing the yield per pass of the desired product. Many of these catalysts, however, have necessitated the use of relatively high reaction temperatures, e.g., above 600° C., and/or low

pressures, generally between about 5 and 25 p.s.i.a. Recently, catalysts of the ferrite family have been proposed for use in oxidative dehydrogenation processes. These catalysts, however, are prepared at relatively high temperatures, i.e., about 850° C. to 1,300° C., and have been found to be stable for only relatively short periods of time at reaction conditions.

In accordance with the present invention, there is provided a process for the oxidative dehydrogenation of hydrocarbons comprising contacting at least one hydrocarbon containing at least 4 carbon atoms and oxygen at a temperature above 250° C. with a catalyst containing as an active catalytic component a single phase, ternary ferrite selected from the class consisting of magnesium chromium ferrite of the composition $Mg Cr Fe O_4$, zinc chromium ferrite of the composition $Zn Cr Fe O_4$, and lanthanum chromium ferrite of the composition $La_{0.8}Cr_{0.65}Fe_{0.55}O_3$ wherein the said magnesium chromium ferrite is present as a partially inverted spinel, said zinc chromium ferrite is present as a spinel, and the said lanthanum chromium ferrite is present as a perovskite and the said active catalytic components, respectively, evidencing characteristic X-ray diffraction patterns as illustrated by the following d spacings and relative intensities:

Magnesium Chromium Ferrite ($MgCrFeO_4$)		Zinc Chromium Ferrite ($ZnCrFeO_4$)		Lanthanum Chromium Ferrite ($La_{0.8}Cr_{0.65}Fe_{0.55}O_3$)	
d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io
4.83	36	4.84	10	3.93	25
2.96	24	2.99	35	2.78	100
2.52	100	2.54	100	2.27	20
2.41	5	2.43	10	1.965	30
2.09	35	2.10	20	1.76	10
1.705	1	1.72	12	1.60	30
1.605	30	1.62	30	1.39	12
1.475	40	1.49	40		

One class of catalysts useful in the present invention are magnesium chromium ferrites containing, as the active components thereof, magnesium, chromium and iron cations in a single phase partially inverted spinel compound. Magnesium has a stronger octahedral site stabilization energy than the trivalent iron, and when these are combined in accordance with the present invention, the result is a partially inverted spinel in which a significant number of the magnesium cations tend to occupy octahedral sites and a corresponding number of iron cations are displaced into tetrahedral sites. Another class of catalysts useful in the present invention are zinc chromium ferrites containing, as the active components thereof zinc, chromium and iron cations in a single phase spinel compound. Another class of catalysts useful in the present invention are lanthanum chromium ferrites containing, as the active components thereof, lanthanum, chromium and iron cations in a single phase perovskite compound. The catalyst can be employed in the form of the homogeneous magnesium chromium ferrite, zinc chromium ferrite, or lanthanum chromium ferrite *per se*, or as a heterogeneous compositions containing a mixture of the oxides of said cations and the single phase partially inverted spinel compound, the single phase spinel compound or the single phase perovskite compound, respectively.

The magnesium chromium ferrite-containing catalyst composition can be represented by the empirical formula $Mg_aCr_bFe_cO_4$ wherein a can vary within the range of 0.1 to 3, b can vary from greater than 0 to less than 2 and c

can vary from greater than 0 to less than 3. In a preferred form of the catalyst composition a can vary within the range of 0.1 to 2.0, b can vary from 0.1 to 1.8 and c can vary from 0.25 to 1.9 while in a more preferred arrangement a can vary from 0.8 to 1.3, b can vary from 0.2 to 1.5 and c can vary from 0.5 to 1.8. In the most preferred form of the catalyst a is 1.0.

The zinc chromium ferrite-containing catalyst composition employed in the present invention can be represented by the empirical formula $Zn_aCr_bFe_cO_4$ wherein a can vary within the range of from 0.1 to 3, b can vary from greater than 0 to less than 2 and c can vary from greater than 0 to less than 3. In a preferred form of the catalyst a can vary within the range of 0.1 to 2.0, b can vary from 0.1 to 1.8 and c can vary from 0.25 to 1.9 while in a more preferred form a can vary from 0.8 to about 1.3, b can vary from 0.2 to 1.5 and c can vary from 0.5 to 1.8. In the most preferred form of the catalyst a is 1.0.

The lanthanum chromium ferrite-containing catalyst composition can be represented by the empirical formula $La_aCr_bFe_cO_3$ wherein a can vary within the range of 0.3 to 1.25, b can vary from 0.1 to 1 and c can vary from 0.1 to 1.25. At the extremes of the ranges set forth herein, the homogeneity of the perovskite compound is not preserved and a mixture of the perovskite compound with oxides of the respective cations is obtained. Although the heterogeneous mixtures of the oxides and the perovskite compounds are active catalysts for oxidative dehydrogenation of hydrocarbons, it is considered preferable to employ substantially homo-

geneous perovskite compounds. Substantially homogeneous perovskite compounds can be obtained within the composition range wherein a can vary from 0.7 to 1, b can vary from 0.1 to 1 and c can vary from 0.1 to 1, with $a+b+c=2$. It is considered preferable, however, that the perovskite compounds have compositions wherein a can range from 0.7 to 1, b can range from 0.5 to 0.75 and c can range from 0.45 to 0.75, with $a+b+c=2$. Optimumly, the catalyst is a single phase perovskite compound having the empirical formula

$$La_{0.8}Cr_{0.65}Fe_{0.55}O_3.$$

In the homogeneous structure all of the elements are located in a single phase magnesium chromium ferrite or zinc chromium ferrite compound. Since magnesium possesses a high octahedral site stabilization energy, a substantial amount of the magnesium will be in octahedral sites and a corresponding amount of iron will be in tetrahedral sites. Since localized irregularities and non-stoichiometric relationships will occur in the lattice of homogeneous magnesium chromium ferrite as actually prepared, a is about 1.0 and the sum of $b+c$ is about 2.0.

In the ideal homogeneous structure of the zinc chromium ferrite all of the tetrahedral sites are filled by zinc because of its low octahedral site stabilization energy and all of the octahedral sites are filled with chromium and iron, therefore a is 1.0 and the sum of $a+b+c$ is 3.0 in this ideal structure. However, this ideal structure is unlikely to be encountered since a minor amount of the zinc will likely end up in octahedral sites and a minor amount of the iron will likely end up in tetrahedral

sites. In view of this, it can be stated that in the actual homogeneous zinc chromium ferrite a is about 1.0, the sum of $b+c$ is about 2.0, and the sum of $a+b+c$ is about 3.0.

In the heterogeneous composition, represented by the empirical formula $Mg_aCr_bFe_cO_4$ or $Zn_aCr_bFe_cO_4$, there will be present the single phase magnesium chromium ferrite or zinc chromium ferrite compound as well as one or more oxides (or combined oxides) of one or more of the constituent cations. For example, if in the empirical composition a is about 3, the catalyst will contain a major amount of magnesium or zinc oxide and a minor amount of a magnesium chromium ferrite or zinc chromium ferrite compound. In this instance the composition will possess catalytic activity due to the magnesium or zinc chromium ferrite compound with magnesium or zinc oxide serving essentially as an inert diluent. Chromium and iron oxides, if present, may not be inert, i.e. they will have some activity for the desired reaction but with lower selectivity to the desired reaction. The empirical composition $MgCrFeO_4$ can represent a homogeneous composition or it can be a heterogeneous mixture of a magnesium chromium ferrite and individual oxides. The homogeneous material can only result when a is 1.0 or about 1.0. When a deviates significantly from 1.0, the material is heterogeneous.

The magnesium chromium ferrite, zinc chromium ferrite and lanthanum chromium ferrite active components of the catalysts employed in the process of the present invention can be identified by their characteristic X-ray diffraction patterns which consist of lines with the following " d " spacings and relative intensities:

Magnesium chromium ferrite ($MgCrFeO_4$)		Zinc chromium ferrite ($ZnCrFeO_4$)		Lanthanum chromium ferrite ($La_{0.8}Cr_{0.65}Fe_{0.55}O_3$)	
d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io
4.83	36	4.84	10	3.93	25
2.96	24	2.99	35	2.78	100
2.52	100	2.54	100	2.27	20
2.41	5	2.43	10	1.965	30
2.09	35	2.10	20	1.76	10
1.705	1	1.72	12	1.60	30
1.605	30	1.62	30	1.39	12
1.475	40	1.49	40		

These patterns correspond to a cubic unit cell. The relative intensities and the "d" values will vary with changes in the relative concentrations of the cations in the structure. Inhomogeneity in the catalyst composition is manifested by additional or doubled lines in the pattern. With some compositions, the cubic structure can become sufficiently distorted to cause other lines to appear, corresponding to a lattice structure with a symmetry lower than that of the cubic lattice.

The magnesium chromium ferrites can be conveniently prepared by employing as starting materials salts of magnesium, chromium and iron, in which salts the metals are contained as cations. Similarly, the zinc chromium ferrites can be conveniently prepared by employing as starting materials salts of zinc, chromium and iron, in which salts the metals are contained as cations. The lanthanum chromium ferrites can be conveniently prepared by employing as starting materials salts of lanthanum, chromium and iron, in which salts the metals are contained as cations. Any such salt of said metals is satisfactory, however, it is preferred to employ inorganic salts of the metals, such as, for example, nitrates, carbonates, acetates and halides. These salts containing the metals as cations are then admixed with a basic reactant in order to precipitate the precursor of the final product. It is necessary to maintain this addition mixture at a high pH-above about 8, and preferably above about 9. It is considered preferable to vigorously stir the metal salts in order to reduce any pH gradients through said addition mixture.

In order to prevent the inclusion in the precursor, and thus in the final product, of any contaminant it is essential that either a volatilizable base or a base containing no deleterious contaminants such as, for example, sodium, be employed. Any base which can be vaporized readily under the conditions used for drying and calcining can be employed, such as, for example, ammonium carbonate, ammonium bicarbonate and ammonium hydroxide. It is considered preferable, however, to employ an aqueous ammonia solution as the volatilizable base.

After precipitation, advantageously the precursor is washed, again at a pH above 8, and preferably above 9, and then dried and calcined. This drying and calcining can effectively be accomplished by any of the techniques well known in the art. Generally, drying can be accomplished at temperatures from 100° C. to 150° C. for a period of from 4 to 60 hours while calcining can be effected at temperatures ranging from 350° C. to 800° C. for a period of from 2 to 16 hours.

It has been found that the magnesium chromium ferrite catalyst can be conveniently prepared by forming aqueous solutions of salts of the respective cations, magnesium, chromium and iron, preferably the nitrate salts thereof, and admixing said solutions with an aqueous ammonium hydroxide solution at a pH above 8, preferably between a pH of from 8.5 to 8.9, thereby co-precipitating the hydroxides of the cations. The resulting precipitate can then be washed, filtered, dried and calcined to yield the finished bulk catalyst.

It has been found that iron hydroxide precipitates from an aqueous solution of

$$Fe(NO_3)_3.9H_2O$$
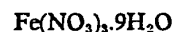
in ammonium hydroxide substantially completely at pH 11.0 to 11.5, while chromium and zinc hydroxides precipitate most completely from an aqueous solution of their nitrates in ammonium hydroxide at a pH of about 9.0. Accordingly, a method for the preparation of zinc chromium ferrite comprises co-precipitating the zinc and chromium hydroxide in ammonium hydroxide at a pH of 8.8 to 9.0 in one container, and precipitating the iron hydroxide separately in ammonium hydroxide at a pH of about 11.3 in a second container. Acetone is added to the zinc-chromium precipitate to hasten the settling of the precipitate, so that it can be washed by decantation of the clear supernatant liquid. After both precipitates have been washed several times by decantation, they are combined, mixed thoroughly, preferably with heating at about 90° C., for several hours. Thereafter, the resulting mixture of the combined precipitates is recovered by filtration, dried at about 120° C. and calcined for 16 hours at about 650° C. to form the zinc chromium ferrite catalyst.

It has been found that both lanthanum and iron hydroxides can be precipitated substantially completely from an aqueous solution of their respective nitrates at a pH of 11.0 to 11.8 employing ammonium hydroxide as the precipitating agent, but both have been found to remain partially in solution at pH less than or equal to 10. Chromium, however, is precipitated most completely from a solution of the nitrate at pH 9.0 to 9.5. Accordingly, a convenient method for the preparation of lanthanum chromium ferrites comprises co-precipitating the lanthanum and iron hydroxides in ammonium hydroxide at a pH of about 11.5 in one reaction vessel, and precipitating the chromium separately in ammonium hydroxide at a pH of 9.0 to 9.5 in a second reaction vessel. After both precipitates have been washed several times by decantation, they are combined, mixed thoroughly, preferably with heating at about 90° C. for several hours. Thereafter, the resulting mixture of the combined precipitates is recovered by filtration,

dried at about 120° C. and calcined for 16 hours at about 650° C. to form the lanthanum chromium ferrite catalyst.

The catalyst can be employed with or without a filler or carrier material and can be pelletized or formed employing conventional techniques. Suitable carrier materials are, for example, rough granular aluminas, zirconias, granular silicon carbide and other similar inert materials. Supported catalysts can be prepared by thoroughly mixing the granular particles of the carrier material with a thick wet slurry of the washed mixture of combined precipitates prior to drying and calcining. The slurried mixture can thereafter be dried at about 120° C. and calcined at about 650° C. to provide granular particles of the supported catalyst.

The process of the present invention is useful in the dehydrogenation of hydrocarbons containing at least four carbon atoms. Preferably, aliphatic and aromatic hydrocarbons are employed such as, for example, mono-olefins, diolefins, cycloaliphatic hydrocarbons, aromatic hydrocarbons and mixtures thereof. Exemplary of such hydrocarbons are butene-1, cis-butene-2, trans-butene-2, 2-methyl butene-3, 2-methyl butene-1, 2-methyl butene-2, buta-diene-1,3, cyclohexene, 2-methyl pentene-1, 2-methyl pentene-2, normal amylenes, other iso-amylenes, and mixtures thereof. For example, the process of the present invention is useful in converting butenes to butadiene-1,3. Still further, the process can be employed to convert normal amylenes to piperylene or iso-amylenes to isoprene. Thus, it can be seen that the process of the present invention is, in general, useful in converting unsaturated hydrocarbons to hydrocarbons of greater unsaturation.

The feed streams can be mixed hydrocarbon streams such as refinery streams or effluents from thermal or catalytic cracking processes. These and other refinery by-product streams which contain normal hydrocarbons and/or ethylenically saturated hydrocarbons are useful feed stocks.

It has been found, for example, that a mixed feed stream containing butene and butane can result in butene conversions of greater than 50 mole per cent with greater than 90 per sent selectivity to butadiene-1,3. It has been found that little or no butane was converted to water and carbon dioxide thereby leaving essentially intact the oxygen needed for the oxidative dehydrogenation of butene to buta-diene. Thus, the process of the present invention can, as an embodiment thereof, be employed as a two-stage process where in a first stage butane is non-oxidatively dehydro-genated to a butane-butene mixture over a suitable catalyst such as, for example, chromia on alumina, and the butene in the resulting mixed effluent stream is converted to buta-diene-1,3, in accordance with the present invention, in a second stage.

Oxygen is fed to the reaction zone suitably in an amount ranging from 0.2 to 2.5 moles of oxygen per mole of hydrocarbon to be de-hydrogenated. Preferably, 0.3 to 1 mole of oxygen per mole of hydrocarbon is employed. In general, it has been found that as the amount of hydrocarbon being fed to the reaction zone is increased relative to the oxygen, the conversion decreases and, to a lesser degree, the selectivity increases, with the result that the yield of the desired product decreases as the oxygen to hydrocarbon ratio decreases. The oxygen can be fed to the reaction as pure oxygen, air, oxygen-enriched air, oxygen mixed with inert diluents and the like. The total amount of oxygen utilized can be introduced into the gaseous mixture entering the reaction zone or can be added to increments at different sections of the reaction zone.

The conversion of the feed stream can be increased by employing a series of reaction zones with provision to introduce additional oxygen between reaction zones. The points of introduction of the additional oxygen are estab-lished to ensure that any unreacted hydrocarbon can react over an area of active catalyst after the supply of oxygen in the initial feed stream has been substantially exhausted. It is impor-tant, however, that the added oxygen be in-timately admixed with the other gases and vapors in the reaction zone prior to exposure of the oxygen-enriched mixture to an area of active catalyst.

The hydrocarbon feed stream is preferably dehydrogenated in the presence of added steam; however, the use of steam is not essen-tial and can be omitted. When employed, it is considered preferable that the reaction mixture contain a quantity of steam ranging from 5 to 30 moles of steam per mole of hydrocarbon to be dehydrogenated and most preferably from 10 to 20 moles of steam per mole of hydrocarbon. In addition to acting as a diluent in the process, the flow rate and inlet tempera-ture of the stream can be regulated to vary the internal reaction temperature.

The dehydrogenation reaction proceeds at temperatures of at least 250° C. Preferably, the reaction is conducted at temperatures be-tween 300° C. and 500° C. although higher temperatures approaching 600° C. or higher can be employed if desired. It is considered advantageous to operate at the lower end of the temperature range, for example, from 250° C. to 350° C., since the amount of carbon dioxide produced at these temperatures is appreciably less than at higher temperatures.

The dehydrogenation reaction can be con-ducted at atmospheric pressure, superatmos-pheric pressure or subatmospheric pressure. The total pressure of the system will normally be about or in excess of atmospheric pressure but generally below 10 atmospheres to avoid the explosive limit of the feed stream. Generally the total pressure will range from 0.7

to 10 p.s.i.g. Preferably the total pressure will be in the range of 0.7 to 5 p.s.i.g. Excellent results have been obtained at about atmospheric pressure.

The process of the present invention can be satisfactorily conducted over a wide range of flow rates. The optimum flow rate is dependent upon the reaction temperature, pressures, catalyst particle size and type of reactor employed, e.g., fluid bed or fixed bed. The gaseous hourly space velocity (GHSV) as used herein is the volume of the total hydrocarbon feed in the form of vapor calculated under standard conditions of temperature and pressure (25° C. and 760 mm. Hg) passed per hour per unit volume of catalyst. Generally, the GHSV will be between 200 and 6,000 with GHSV between 450 and 2,000 considered most preferable.

The dehydrogenation reaction zone can be of the fixed bed or fluid bed type. Conventional reactors for the production of unsaturated hydrocarbons are satisfactory. The reactor can either be packed with particulate catalyst, per se, or the catalyst can be deposited on a carrier or support medium as hereinabove described. Other methods can similarly be employed to introduce the catalyst into the reaction zone; for example, the reaction zone itself can be coated with the catalyst or the catalyst in the form of wires, mesh, shreds, tablets and the like can be packed within the reactor.

Although not essential, the catalysts employed in the present invention can be activated by oxidizing and reducing the catalysts in the following sequence: Catalyst is oxidized by passing a stream containing about one part oxygen to about four parts inert diluent such as steam, helium, nitrogen and the like, over the catalyst at temperatures between 400° C. and 600° C., preferably about 500° C. for about 30 minutes. Thereafter, a feed stream comprised of steam, hydrocarbon and oxygen is passed over the catalyst in a gas volume ratio of about 10/1/1, respectively, although the amount of each component can be varied without adverse effect. The feed stream is passed over the catalyst at temperatures of 300° C. to 500° C., preferably at 400° C., for about 30 minutes. Thereafter, the oxidation step is repeated as described above, followed by reaction with the feed stream described above having a gas volume ratio of about 30/3/1, respectively, although again this ratio can be varied without adverse effect. In the case of the magnesium or zinc chromium ferrite catalyst, the oxidation step described hereinabove is again repeated. In the case of the lanthanum chromium ferrite catalyst the entire activation sequence described hereinabove is twice repeated. Finally the catalyst is reduced through use of any reducing gas such as hydrogen, carbon monoxide or hydrocarbons. Most conveniently a hydrocarbon such as butene can be employed as the reducing agent particularly in instances wherein butene is the hydrocarbon to be dehydrogenated simply by stopping the flow of oxygen. Thus, reducing of the catalyst is accomplished by passing butene or other similar hydrocarbon reducing gas in an inert diluent such as steam, helium and the like over the catalyst at temperatures between 400° C. and 600° C., preferably at about 500° C., for about 30 minutes. Alternatively, the catalyst can be activated in situ by passing the reactant feed stream over the unactivated catalyst; however, in such case, the activation takes place over a substantial period of time. Thereafter, the active catalyst of the present invention is obtained, providing higher conversion and selectivity to the desired unsaturated hydrocarbon together with lower isomerization activity. This superior performance is maintained at temperatures as low as about 325° C. with the additional advantage that the amount of carbon dioxide produced is less at such low temperatures than at the higher temperatures.

Examples.

The following examples are to further illustrate the present invention and should not be considered as imposing any limitations on the scope of the invention. Unless otherwise specified, all percentages and parts are by weight.

Example 1.

A magnesium chromium ferrite catalyst was prepared in the following manner: 76.8 gm. of $Mg(NO_3)_2.6H_2O$, 121.2 gm.
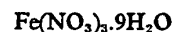
$$Fe(NO_3)_3.9H_2O$$

and 120 gm. $Cr(NO_3)_3.9H_2O$ were dissolved in 1,000 ml. of distilled water forming a mixed cation solution. 250 ml. concentrated NH_4OH was added to 750 ml. of distilled water forming a base solution. The base solution was added to a vessel containing 1,000 ml. of distilled water until a pH of 8.0 was attained. Thereafter, the mixed cation solution and the base solution were simultaneously, slowly added to the vessel with vigorous stirring, adjusting the rate of addition of the base solution to maintain a pH of 8.5 to 9.0 in the vessel. The final pH was between 8.9 to 9.0. The time required for the simultaneous addition was about 30 minutes, and a volume of 720 ml. of the base solution was employed. The resulting precipitate was allowed to settle overnight, and the clear supernatant liquid was thereafter decanted. Additional water was added and the decantation procedure repeated until the precipitate had been washed with at least two or three complete changes of water. The washed precipitate was filtered, dried at 120° C. and calcined at 650° C. for 16 hours.

X-ray diffraction analysis of the calcined product indicated a single phase with a well-

ordered partially inverted spinel structure corresponding to MgCrFeO$_4$.

4.1 gm. of MgCrFeO$_4$ prepared in the manner described above was admixed with an equal volume of silicon carbide and loaded into a reactor consisting of a 22″ × 3/4″ stainless steel tube with a 22″ × 15 mm. Vycor linear. The reactor was heated by means of a 13″ Hevi-Duty tube furnace and the furnace temperature was controlled by Thermo Electronic Temperature regulators. Temperatures within the catalyst bed were determined by means of a 1/16″ concentric stainless steel thermocouple well running the length of the reactor. The void space above and below the catalyst bed was filled with coarse particles of silicon carbide. The first 5″ of the reactor were used to preheat the inlet gases to reaction temperatures.

The catalyst was activated by oxidizing the catalyst with a 1.5/1 mixture of helium and oxygen for 30 minutes at 500° C. at a GHSV of 1,500 hr. $^{-1}$. The catalyst was further conditioned by reaction at 400° C. with a feed stream consisting of a 10/1/1 mixture based on a gas volume of steam, butene-2 and oxygen. The reaction was carried out for 30 minutes at a total GHSV of 5,500 hr.$^{-1}$. After the reaction, the catalyst was reoxidized as described above and thereafter the reaction was continued at 400° C. with a 30/3/1 mixture based on gas volume of steam, butene-2 and oxygen. The reaction was conducted for 30 minutes at a total GHSV of 4,200 hr.$^{-1}$. The catalyst was again oxidized as described above and then reduced at 500° C. with a 10/1 mixture of helium and butene-2 for 30 minutes at a total GHSV of 5,000 hr.$^{-1}$. Although the oxidation and reduction steps described herein have been conducted with helium as the inert diluent nitrogen, steam, or any other similar inert diluent can likewise be employed.

The results obtained with the catalyst prior to activation and after activation are summarized in Table 1 below.

TABLE 1

T(°C)	O_2/C_4	Feed Stream		Conversion (Mole %)	C_4H_6 (Mole %)	CO_2 (Mole %)	Yield of Butadiene (Mole %)
		Steam Butene	GHSV (Butene)				
Prior to Activation							
400	1	10	450	54	72	28	39
400	0.33	10	450	19	72	28	14
After Activation							
350	1	10	450	77	80	20	61
400	1	10	450	79	82	18	65
400	0.5	10	450	51	90	10	46
350	1	10	450	76	86	14	65
350	0.67	10	450	64	90	10	58
325	1	10	450	82	84	16	69
325	0.67	10	450	61	90	10	55
325	1	20	450	80	86	14	69
325	0.67	20	450	41	92	8	38
325	0.67	14	675	65	90	10	58
325	0.67	10	900	76	91	9	69
325	0.67	8	1,125	75	88	12	66
325	0.67	7	1,350	70	88	12	62
325	0.67	17	1,350	71	90	10	64
400	1	10	450	78	82	18	64

Example 2.

To further illustrate the superior perform-
ance of the magnesium chromium ferrite com-
positions employed in the present invention, the
oxidative dehydrogenation process as des-
cribed herein was conducted employing dif-
ferent magnesium chromium ferrite composi-
tions and, for comparative purposes, oxides of
the cations employed in the present invention.
Table 2 shown below summarizes the results
obtained employing the catalysts of the pre-
sent invention and magnesium ferrite, mag-
nesium chromite, iron chromite and ferric
oxide.

TABLE 2

Catalyst Composition	T(°C)	O_2/C_4H_8	Conversion (Mole %)	C_4H_6 (Mole %)	CO_2 (Mole %)	Yield C_4H_6 (Mole %)
$MgCrFeO_4$	400	1	79	82	18	65
	400	0.5	51	90	10	46
	325	0.67	64	90	10	58
$MgCr_{0.5}Fe_{1.5}O_4$	400	1	67	85	15	57
	400	0.5	38	86	14	33
	325	0.67	44	85	15	37
$MgFe_2O_4$	400	1	46	84	16	37
	400	0.5	26	90	10	24
	325	0.67	7	93	7	6
$MgCr_2O_4$	400	1	29	38	62	11
	400	0.5	16	42	58	7
$FeCrO_3$	400	1	41	62	38	25
	400	0.33	26	85	15	22
	400	1	55	76	24	42
	400	0.50	36	85	15	31
	400	0.33	30	87	13	26
Fe_2O_3	400	1	34	55	45	19
	400	0.33	12	61	39	7
	400	1	31	56	44	17
	400	0.50	19	57	43	11
	400	0.33	12	52	48	6

Example 3.

The following example illustrates the effect of the conjoint use of n-butane in the oxidative dehydrogenation of butene-2 to butadiene employing the magnesium chromium ferrite catalyst of the present invention. The process em-ployed was substantially similar to that des-cribed in Example 1, except that the feed stream contained a combined butane-butene stream. The results obtained are summarized in Table 3 below.

TABLE 3

Effect of n-Butane on the Oxidative Dehydrogenation of Butene-2 to Butadiene

Catalyst Composition	T(°C)	Butane Butene	Oxygen Butene	Conversion (Mole %)	Selectivity to C_4H_6 (Mole %)	CO_2 (Mole %)	Yield C_4H_6 (Mole %)
$MgCr_{0.5}Fe_{1.5}O_4$	400	0	1	66	81	19	53
	400	3	1	69	82	18	56
	400	6.7	1	68	84	16	57
	350	6.7	0.67	57	91	9	52
	325	0	0.67	54	85	15	46
	325	1	0.67	53	90	10	48
	325	3	0.67	23	92	8	21
	325	6.7	0.67	15	94	6	14
	325	0(a)	0.67	53	90	10	48

(a) Steam/C_4H_8 = 13.5/1

Example 4.

A zinc chromium ferrite catalyst was pre-pared in the following manner: 74.5 gm. of $Zn(NO_3)_2.6H_2O$ were dissolved in 750 ml. of distilled water and concurrently 100 gm. of $Cr(NO_3)_3.9H_2O$ were dissolved in 2,000 ml. of distilled water. The two resulting solutions were combined in a 2 gallon vessel. A solution comprising 100 ml. of concentrated ammonium hydroxide in 400 ml. of distilled water was slowly added to the vessel with vigorous stir-ring until a pH of 8.8 was attained. Stirring was continued for about 20 minutes when approximately 350 cc. of acetone were added to the vessel. Stirring was continued briefly. After standing, a clear supernatant liquid appeared which was decanted. Additional water plus acetone was added and the decantation procedure was repeated until the precipitate had been washed with at least two or three complete changes of water. 114 Grams of $Fe(NO_3)_3.9H_2O$ were dissolved in 1,500 ml. of distilled water. 500 ml. of distilled water were added to a 2 gallon vessel and an ammonium hydroxide solution prepared as described above was added until a pH of 11.3 was attained. The $Fe(NO_3)_3.9H_2O$ solution and additional ammonium hydroxide solution were slowly added to the 2 gallon vessel with vigorous stirring maintaining a pH of 11.2

to 11.3 in said vessel. The resulting precipi-tate was allowed to stand and was thereafter washed by decantation of the clear supernatant liquid until at least three complete changes of water had been made. The washed precipitate was combined with the washed zinc-chromium precipitate and the combined precipitate was heated to approximately 90° C. and stirred from two to three hours. The combined pre-cipitate was filtered, dried at 120° C. and calcined at 650° C. for 16 hours.

X-ray diffraction analysis of the calcined product indicated that the major phase was a mixed cation oxide with the spinel structure and minor amounts of uncombined ZnO and $(CrFe)_2O_3$ were also present. X-ray fluores-cence analysis indicated that the three cations were also present in the proportions

Zn : Cr : Fe-1 : 1 : 1.

4.1 Grams of granular $ZnCrFeO_4$ prepared in the manner described above were admixed with an equal volume of silicon carbide and loaded into the reactor and activated as des-cribed in Example 1.

The results obtained with the catalyst prior to activation and after activation are sum-marized below.

Catalyst State	T °C	O_2/C_4	GHSV (Butene-2)	Conversion Mole %	Selectivity Mole %	Yield C_4H_6 Mole %
Non-activated	400	1	450	52	72	40
Activated	400	1	450	60	80	48
	325	0.67	450	58	91	53

Example 5.

Three and one tenth grams of a catalyst with a composition of $Zn_{0.75}CrFe_{1.25}O_4$ was treated as in Example 4.

Catalyst State	T °C	O_2/C_4	GHSV (Butene-2)	Conversion Mole %	Selectivity Mole %	Yield C_4H_6 Mole %
Non-activated	400	1	450	59	74	44
Activated	400	1	450	64	81	52
	325	0.67	1,350	63	89	56

Example 6.
Five and three tenths grams of a catalyst with a composition of $ZnCr_{0.25}Fe_{1.75}O_4$ was treated as in Example 4.

Catalyst State	T°C	O_2/C_4	GHSV (Butene-2)	Conversion Mole %	Selectivity Mole %	Yield C_4H_6 Mole %
Non-activated	400	1	450	61	76	46
Activated	400	1	450	71	81	58
	325	0.67	450	64	89	57

Example 7.
41 Grams of a catalyst of composition $ZnCrFeO_4$ was mixed with silicon carbide and charged into a stainless steel reactor 32 inches 10 in length and one inch in diameter. The reactor was provided with three zones with both electrical heating and air cooling, plus two preheat zones. Reaction temperatures were monitored by means of a 1/4 inch thermocouple well running the length of the reactor. 15 The catalyst was given a pretreatment similar to Example 4.

T°F.	$\dfrac{O_2}{C_4H_8}$	$\dfrac{Steam}{Butene}$	GHSV (Butene)	Conversion Mole %	Selectivity Mole %
900	0.5	20	2000	40	91

Example 8.
20   70 Grams of a catalyst of composition $ZnCrFeO_4$ which was calcined in air at a temperature of 875° C. was treated as in Example 7.

T°F.	$\dfrac{O_2}{C_4H_8}$	$\dfrac{Steam}{C_4H_8}$	GHSV (Butene)	Conversion Mole %	Selectivity Mole %
720	0.11	10	252	87	92
680	0.91	10	252	52	94

25   Example 9.
To illustrate the superior performance of the zinc chromium ferrite catalyst employed in the present invention, the oxidative dehydrogenation process as described herein was conducted with other oxides of the cations em-
30 ployed in the catalyst of the present invention. Table 4 shown below summarizes the results obtained employing the following catalysts: zinc ferrite, zinc chromite, iron chromite and ferric oxide. 35

TABLE 4

Catalyst	Reaction Temperature (°C.)	O₂/C₄H₈	Steam/C₄H₈	GHSV	Conversion Mole %	C₄H₈ Converted to CO₂ Mole %	Selectivity to C₄H₆ Mole %	Yield C₄H₆ Mole %
ZnFe₂O₄	400	0.33	10	450	27	13	87	23 (a)
	400	0.33	10	450	25	13	87	22 (b)
	325	1	10	450	24	10	90	22 (b)
	325	0.67	10	450	20	8	92	18 (b)
ZnCr₂O₄	400	1	10	450	32	68	31	10 (a)
	400	0.33	10	450	12	60	38	5 (a)
	400	1	10	450	31	58	39	12 (b)
	400	0.5	10	450	16	63	36	6 (b)
	400	0.33	10	450	12	57	41	5 (b)
FeCrO₃	400	1	10	450	41	38	62	25 (a)
	400	0.33	10	450	26	15	85	22 (a)
	400	1	10	450	55	24	76	42 (b)
	400	0.5	10	450	36	15	85	31 (b)
	400	0.33	10	450	30	13	87	26 (b)
Fe₂O₃	400	1	10	450	34	45	55	19 (b)
	400	0.33	10	450	12	39	61	7 (b)
	400	1	10	450	31	44	56	17 (b)
	400	0.5	10	450	18	43	57	11 (b)
	400	0.33	10	450	12	48	52	6 (b)

(a) Catalyst activated in stream of He : O₂ : 4 : 1 at 500°C. for 30 minutes prior to first run.

(b) Catalyst treated as in (a) and then reduced in stream of butene (normal feed stream without oxygen) at 500°C. for 30 minutes prior to first run.

Example 10.

Employing the process described in Example 4, several zinc chromium ferrite catalysts were prepared and employed in the oxidative dehydrogenation process of the invention. The results obtained thereby are summarized in Table 5 below.

TABLE 5

Catalyst	Reaction temperature (°C.)	$\dfrac{O_2}{C_4H_8}$	Steam $\dfrac{}{C_4H_8}$	GHSV	Conversion Mole %	C_4H_8 Converted to CO_2 Mole %	Selectivity to C_4H_6 Mole %	Yield C_4H_6 Mole %
$ZnCrFeO_4$	400	1	10	450	52	24	76	40 (a)
	350	1	10	450	65	19	81	53 (b)
	325	1	10	450	66	17	83	55 (b)
	325	0.67	10	450	58	9	91	53 (b)
	300	1	10	450	67	16	84	56 (b)
	325	1	10	450	62	18	82	51 (c)
$Zn_{0.7}CrFe_{1.3}O_3$	400	1	10	450	59	26	74	44 (a)
	400	1	10	450	64	19	81	52 (b)
	400	0.50	10	450	47	12	88	41 (b)
	400	0.37	10	450	38	8	91	34 (b)
	325	1	10	450	66	18	82	54 (b)
	300	1	10	450	66	19	81	53 (b)
	325	1	10	450	67	19	81	54 (c)
$Zn_{0.8}Cr_{0.35}Fe_{1.65}O_4$	400	1	10	450	63	25	75	47 (a)
	325	1	10	450	67	21	79	53 (b)
	325	0.67	10	450	57	14	86	49 (b)
	300	0.67	10	450	46	10	90	41 (b)
$Zn_{0.8}Cr_{0.5}Fe_{1.7}O_4$	400	1	10	450	66	26	74	49 (a)
	325	1	10	450	70	17	83	58 (b)
	325	0.67	10	450	59	11	89	52 (b)
	300	0.67	10	450	34	8	92	31 (b)
	300	1	10	450	72	18	82	59 (b)
	325	1	10	450	70	18	82	57 (c)
	325	0.67	10	450	60	12	88	53 (c)

TABLE 5 (Continued)

Catalyst	Reaction Temperature (°C.)	O_2 / C_4H_8	Steam / C_4H_8	GHSV	Conversion Mole %	C_4H_8 Converted to CO_2 Mole %	Selectivity to C_4H_6 Mole %	Yield C_4H_6 Mole %
$ZnCr_{0.25}Fe_{1.75}O_4$	400	1	10	450	45	22	78	35 (b)
	400	1	10	450	61	19	81	49 (b)
	325	0.67	10	450	56	10	90	50 (b)
	375	0.67	10	450	52	12	88	46 (b)
	325	1	10	450	55	13	87	48 (b)

(a) Catalyst activated in stream of He : O_2 : : 4 : 1 at 500°C. for 30 minutes prior to first run.

(b) Catalyst treated as in (a) and then reduced in stream of butene (normal feed stream without oxygen) at 500°C. for 30 minutes prior to first run.

Example 11.

The following Example illustrates the effect of n-butane on the oxidative dehydrogenation of butene-2 to butadiene employing the zinc chromium ferrite catalyst of the present invention. The process employed was substantially similar to that described in Example 4, except that the feed stream contained a combined butane/butene stream. The results obtained are summarized in Table 6 below.

TABLE 6

Catalyst Composition	T°C.	Butane/Butene	Oxygen/Butene	Conversion Mole %	Selectivity to C_4H_8 Mole %	CO_2 Mole %	Yield C_4H_6 Mole %
$ZnCrFeO_4$	400	0	1	60	79	21	47
	400	3	1	67	81	19	53
	400	6.7	1	70	85	15	60
	350	6.7	0.67	66	93	7	61
	325	0	0.67	56	87	13	49
	325	1	0.67	49	94	6	46
	325	3	0.67	53	94	6	50
	325	6.7	0.67	39	93	7	36
	325	0(a)	0.67	50	93	7	46
$ZnCr_{0.1}Fe_{1.9}O_4$	400	0	1	67	77	23	52
	400	3	1	70	82	18	57
	400	6.7	1	69	85	15	59
	350	6.7	0.67	61	92	8	56
	325	0	0.67	58	89	11	52
	325	1	0.67	54	93	7	50
	325	3	0.67	49	92	8	45
	325	6.7	0.67	39	92	8	36
	325	0(a)	0.67	52	91	9	47
$ZnCr_{0.25}Fe_{1.75}O_4$	400	0	1	71	81	19	58
	400	6.7	1	74	85	15	63
	350	6.7	0.67	68	91	9	62
	325	0	0.67	59	86	14	51
	325	1	0.67	62	89	11	55
	325	3	0.67	69	91	9	63
	325	6.7	0.67	64	91	9	58
	325	0(a)	0.67	64	89	11	57

(a) Steam increased to keep butane partial pressure the same as when $\dfrac{\text{Butane}}{\text{Butene}} = 6.7$

Example 12.

I lanthanum chromium ferrite catalyst was prepared in the following manner:

242.4 gm. of $Fe(NO_3)_3.9H_2O$ and 216.5 gm. of $La(NO_3)_3.6H_2O$ were dissolved in 1,000 ml. of distilled water in a first beaker. 1,000 ml. of distilled water were charged to a 2 gallon vessel and about 700 ml. of 7% ammonium hydroxide solution were added to said vessel to impart to the resulting aqueous solution a pH of 11.5. 500 ml. of concentrated ammonium hydroxide were admixed with 500 ml. of distilled water in a second beaker. The solutions contained in the first and second beakers were slowly added to said 2 gallon vessel, with vigorous agitation. The rate of addition of the solution in the second beaker was adjusted to maintain a pH of 11 in the vessel at all times.

60 gm. $Cr(NO_3)_3.9H_2O$ were dissolved in 500 ml. of distilled water in a third beaker. 1,000 ml. of concentrated ammonium hydroxide were charged to a fourth beaker. 1,000 ml. of distilled water were charged to a second 2 gallon vessel to which was added ammonium hydroxide until a pH of 9.5 was attained. The solutions contained in said third and fourth beakers were slowly added to said second vessel, with vigorous agitation. The rate of addition of the concentrated ammonium hydroxide was adjusted to maintain a pH between 9.0 to 9.5 in said vessel at all times.

The resulting precipitates were allowed to settle overnight and the clear supernatant liquid was decanted from each. The precipitates were then thoroughly admixed and heated to about 90° C. with constant stirring, until the volume was reduced to about 1,100 ml. The combined precipitate was then filtered, dried at 120° C. and calcined for 16 hours at 650° C.

X-ray diffraction analysis of the calcined product indicated a single phase with the perovskite structure. X-ray fluorescence analysis indicated a composition corresponding to $La_{0.8}Cr_{0.2}FeO_3$.

Example 13.

In this example, a 4-cubic centimeter volume of 10—20 mesh lanthanum chromium ferrite catalyst particles of this invention were premixed with 4 cubic centimeters of 10—20 mesh silicon carbide particles. The catalyst was the same as that employed in Example 12. When charged into the reactor, this gave a catalyst bed 3″ in length. The reactor consisted of a 22″ × 3/4″ stainless steel tube with a 22″ × 15 mm. Vycor liner heated by means of a 13″ Hevi-Duty tube furnace. The furnace temperature was controlled by Thermo Electronic Temperature regulators. Temperatures within the catalyst bed were determined by means of a 1/16″ concentric stainless steel thermocouple well running the length of the reactor. The void space above and below the catalyst bed was filled with coarse particles of silicon carbide. The first five inches of the reactor were used to preheat the inlet gases to reaction temperature.

The catalyst was activated by oxidizing the catalyst with a 1.5/1 mixture of helium and oxygen for 30 minutes at 500° C. at a total GHSV of 1,500 hr.$^{-1}$. Conditioning of the catalyst was continued by reacting at 400° C. with a feed stream consisting of a 10/1/1 mixture based on a gas volume of steam, butene-2 and oxygen. The reaction was carried out for 30 minutes at a total GHSV of 5,400 hr.$^{-1}$. After the reaction, the catalyst was reoxidized as described above and thereafter the reaction was continued at 400° C. with a 30/3/1 mixture based on gas volume of steam, butene-2 and oxygen. The reaction was conducted for 30 minutes at a total GHSV of 5,200 hr.$^{-1}$. The sequence as described above was repeated twice and then the catalyst was reduced at 500°C. with a 10/1 mixture of helium and butene-2 for 30 minutes at a total GHSV of 5,000 hr.$^{-1}$. Although the oxidation and reduction steps described herein have been conducted with helium as the inert diluent nitrogen, steam, or any other similar inert diluent can likewise be employed.

The result obtained with the catalyst prior to complete activation and after activation are summarized in Table 7 below:

TABLE 7

(Catalyst not pretreated before runs)

Run #	T(°C.)	%C$_4$	O$_2$/C$_4$	Steam/C$_4$	GHSV	Conversion (Mole %)	Selectivity to Butadiene (Mole %)	Yield (Mole %)
1 (a)	400	8.2	1	10	5400	38	45	17
2 (a)	400	8.5	0.33	10	5200	14	65	12
3 (a)	450	8.2	1	10	5400	32	48	15
4 (a)	450	8.5	0.33	10	5200	14	70	13
5 (a)	500	8.2	1	10	5400	34	42	14
6 (a)	500	8.5	0.33	10	5200	34	61	13
			Reduced in Butene 30 minutes at 500°C.					
7 (b)	400	8.2	1	10	5400	54	76	41
8 (b)	400	8.5	0.5	10	5200	33	84	28
9 (b)	400	8.5	0.33	10	5200	29	86	25
			Re-oxidized and reduced in Butene 30 minutes at 500°C.					
10 (b)	400	8.2	1	10	5400	56	74	41
11 (b)	400	8.5	0.5	10	5200	37	84	31

(a) Catalyst oxidized between runs.

(b) Catalyst not oxidized between runs.

Example 14.

To illustrate the superior performance of the lanthanum chromium ferrite catalyst employed in the present invention, the oxidative dehydrogenation process as described herein was conducted with other oxides of the cations employed in the catalyst of the present invention. Table 8 shown below summarizes the results obtained employing the following catalysts: lanthanum ferrite, lanthanum chromite, iron chromite and ferric oxide:

TABLE 8

(Steam/C_4 ratio = 10; GHS = 5,400 throughout)

Catalyst Composition	T(°C.)	Feed Stream		Conversion (Mole %)	Selectivity to Butadiene (Mole %)	CO_2 (Mole %)	Yield (Mole %)
		%C_4	O_2/C_4				
$La_{0.7}CrFe_{0.3}O_3$	400	7.5 (c)	1	42	73	25	31
	375	7.5 (c)	1	41	67	33	27
	350	7.5 (c)	1	41	68	31	28
	300	7.5 (c)	1	42	73	27	31
	400	7.5 (d)	1	42	73	27	31
$La_{0.8}Cr_{0.65}Fe_{0.65}O_3$	400	7.5 (c)	1	50	76	23	38
	375	7.5 (c)	1	52	70	29	36
	350	7.5 (c)	1	51	73	27	37
	300	7.5 (c)	1	54	75	25	40
	400	7.5 (d)	1	48	77	22	37
$LaFeO_3$	400	7.5 (c)	1	32	54	44	17
	375	7.5 (c)	1	31	56	44	17
$LaCrO_3$	400	7.5 (c)	1	19	12	84	2
	375	7.5 (c)	1	17	12	88	2
$FeCrO_3$	400	8.2 (a)	0.33	41	62	38	25
	400	8.2 (a)	1	26	85	15	22
	400	8.2 (b)	0.50	55	76	24	42
	400	8.2 (b)	0.33	36	85	15	31
	400	8.2 (b)	1	30	87	13	26
Fe_2O_3	400	8.2 (b)	0.33	34	55	45	19
	400	8.2 (b)	1	12	61	39	7
	400	8.2 (b)	1	31	56	44	17
	400	8.2 (b)	0.50	19	57	43	11
	400	8.2 (b)	0.33	12	52	48	6

(a) Catalyst activated in stream of $He : O_2 :: 4 : 1$ at 500°C. for 30 minutes prior to first run.

(b) Catalyst treated as in (a) and then reduced in stream of butene (normal feed stream without oxygen) at 500°C. for 30 minutes prior to first run.

(c) Feed was butene-1.

(d) Feed was butene-2.

WHAT WE CLAIM IS:—

1. Process for the oxidative dehydrogenation of hydrocarbons which comprises contacting at least one hydrocarbon containing at least 4 carbon atoms and oxygen at a temperature above 250° C. with a catalyst containing as an active catalytic component a single phase, ternary ferrite selected from the class consisting of magnesium chromium ferrite of the composition Mg Cr Fe O_4, zinc chromium ferrite of the composition Zn Cr Fe O_4, and lanthanum chromium ferrite of the composition $La_{0.8}Cr_{0.65}Fe_{0.55}O_3$ wherein the said magnesium chromium ferrite is present as a partially inverted spinel, said zinc chromium ferrite is present as a spinel, and the said lanthanum chromium ferrite is present as a perovskite and the said active catalytic components, respectively evidencing characteristic X-ray diffraction patterns as illustrated by the following d spacings and relative intensities:

Magnesium Chromium Ferrite (MgCrFeO$_4$)		Zinc Chromium Ferrite (ZnCrFeO$_4$)		Lanthanum Chromium Ferrite (La$_{0.8}$Cr$_{0.65}$Fe$_{0.55}$O$_3$)	
d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io
4.83	36	4.84	10	3.93	25
2.96	24	2.99	35	2.78	100
2.52	100	2.54	100	2.27	20
2.41	5	2.43	10	1.965	30
2.09	35	2.10	20	1.76	10
1.705	1	1.72	12	1.60	30
1.605	30	1.62	30	1.39	12
1.475	40	1.49	40		

2. Process according to claim 1, in which the catalyst is a magnesium or zinc chromium ferrite-containing composition having the empirical formula Mg$_a$Cr$_b$Fe$_c$O$_4$ or

Zn$_a$Cr$_b$Fe$_c$O$_4$,

respectively, wherein a ranges from 0.1 to 3, b ranges from greater than 0 to less than 2 and c ranges from greater than 0 to less than 3.

3. Process according to claim 2, in which a ranges from 0.1 to 2, b ranges from 0.1 to 1.8 and c ranges from 0.25 to 1.9.

4. Process according to claim 2, in which in the magnesium chromium ferrite-containing catalyst composition a ranges from 0.8 to 1.3, b ranges from 0.2 to 1.5 and c ranges from 0.5 to 1.8.

5. Process according to claim 2, in which the magnesium chromium ferrite-containing catalyst composition has the empirical formula MgCr$_b$Fe$_c$O$_4$ wherein b + c = about 2.

6. Process according to claim 2, in which the magnesium chromium ferrite catalyst is MgCrFeO$_4$ per se.

7. Process according to claim 2, in which in the zinc chromium ferrite-containing catalyst composition a ranges from 0.8 to 1.3, b ranges from 0.2 to 1.5 and c ranges from 0.5 to 1.8.

8. Process according to any one of claims 2, 3 and 7, in which in the zinc chromium ferrite-containing catalyst composition a is about 1 and the sum of b + c is about 2.

9. Process according to claim 2, in which the zinc chromium ferrite catalyst is ZnCrFeO$_4$ per se.

10. Process according to claim 1, in which the catalyst is a lanthanum chromium ferrite-containing composition having the empirical formula La$_a$Cr$_b$Fe$_c$O$_3$ wherein a ranges from 0.3 to 1.25, b ranges from 0.1 to 1 and c ranges from 0.1 to 1.25 wherein a + b + c = 2.

11. Process according to claim 10, in which in the lanthanum chromium ferrite-containing catalyst composition a ranges from 0.7 to 1, b ranges from 0.1 to 1 and c ranges from 0.1 to 1, and a + b + c = 2.

12. Process according to claim 10, in which in the lanthanum chromium ferrite-containing catalyst composition a ranges from 0.7 to 1,

b ranges from 0.5 to 0.75 and c ranges from 0.45 to 0.75, and $a+b+c=2$.

13. Process according to claim 10, in which the lanthanum chromium ferrite catalyst is $La_{0.8}Cr_{0.65}Fe_{0.55}O_3$ per se.

14. Process according to any one of the preceding claims, in which the catalyst is activated.

15. A process as claimed in claim 14 in which the catalyst is a magnesium or zinc chromium ferrite-containing catalyst composition and in which the catalyst is activated by (a) contacting the catalyst with an oxidising stream comprising oxygen and an inert diluent at temperatures of from 400° C. to 600° C. for a period of time sufficient to oxidize the catalyst; (b) passing a feed stream of steam, hydrocarbon and oxygen over the catalyst at temperatures of from 300° C. to 500° C. for about 30 minutes, repeating the steps (a) and (b), (c) reoxidising the catalyst as in step (a) and reducing the catalyst by passing a reducing stream over the catalyst comprising a reducing gas and an inert diluent at a temperature of from 400° C. to 600° C. for about 30 minutes.

16. Process according to claim 14, in which the catalyst is a lanthanum chromium ferrite-containing catalyst composition and in which the catalyst is activated by (a) contacting said catalyst with an oxidising stream comprising oxygen and an inert diluent at temperatures of from 400° C. to 600° C. for a period of time sufficient to oxidize said catalyst; (b) passing a feed stream of steam, hydrocarbon and oxygen over the catalyst at temperatures of from 300° C. to 500° C. for about 30 minutes; repeating the steps (a) and (b) twice more; and (c) reducing the catalyst by passing a reducing stream over the catalyst comprising a reducing gas and an inert diluent at a temperature of from 400° C. to 600° C. for about 30 minutes.

17. Process according to any one of the preceding claims, in which from 0.2 to 2.5 moles of oxygen are contacted per mole of the hydrocarbon.

18. Process according to claim 17, in which from 0.3 to 1 mole of oxygen are contacted per mole of hydrocarbon.

19. Process according to claim 17 or 18, in which from 5 to 30 moles of steam per mole of hydrocarbon are included in the reaction mixture.

20. Process according to claim 19, in which from 10 to 20 moles of steam are contacted per mole of hydrocarbon.

21. Process according to any one of the preceding claims, in which the oxidative dehydrogenation is conducted at temperatures of from 300° C. to 500° C.

22. Process according to any one of the preceding claims, in which the hydrocarbon comprises butene.

23. Process according to claim 22, in which the hydrocarbon comprises a mixture of butene and butane.

24. Process according to any one of claims 1 to 21, in which the hydrocarbon comprises an isoamylene.

25. Process for the oxidative dehydrogenation of hydrocarbons according to claim 1 and substantially as herein described with reference to the Examples 1 to 8, 10, 11, 13 and 14.

26. A hydrocarbon when produced by the dehydrogenation process according to any one of the preceding claims.

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Reference has been directed in pursuance of Section 9, subsection (1) of the Patents Act 1949, to patent No. 1,152,484.

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